

## **Effect of Biodegradation on MCHM Released to the Elk River, West Virginia**

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As a result of the estimated 10,000-gallon spill of crude 4-methylcyclohexanemethanol (MCHM) that drained from a storage tank and entered the Elk River in West Virginia in January 2014, information on the environmental fate of this chemical mixture is critically needed. Little appears to be known about the transport properties and degradation reactions of MCHM, despite its common use as a frothing agent to clean coal and subsequent release to the environment in wash water. The relatively low solubility of MCHM in water and the lipophilic nature of this compound, as suggested by its chemical structure, indicate that sorption of MCHM to soils and sediment beneath the storage tank and in the bottom sediments of the Elk River could slow its transport and complete flushing from the area impacted by the spill. Slow release of MCHM from dissolution of pools of the compound and sorbed material could provide a long-term source of contaminants to water. For many organic compounds, biodegradation reactions are the primary mechanism for attenuation and potential complete destruction of the contaminant in soils, groundwater, and bottom sediments. Alternatively, biodegradation sometimes produces intermediate compounds that are more soluble and toxic than the parent compound (i.e. production of vinyl chloride from incomplete degradation of trichloroethylene). Defining biodegradation processes and products, therefore, is important to provide an understanding of the fate and toxicity of the MCHM released in this spill and at coal washing facilities. We propose to evaluate the biodegradation of crude MCHM and pure MCHM in laboratory microcosms using sediment exposed to crude MCHM at the spill site by the Elk River, West Virginia.

MCHM is a saturated alicyclic primary alcohol with a methyl (CH<sub>3</sub>) and hydroxymethyl

(CH<sub>2</sub>OH) group on the cyclohexane ring, which can give *cis* and *trans* isomers depending on the positions of these groups. The relative amounts of the isomers and other components in crude MCHM commercial mixtures can vary with supplier. Eastman lists MCHM as consisting of 68-89 percent MCHM, 4-10 percent water, 5 percent methyl 4-methylcyclohexanecarboxylate, 1 percent dimethyl 1,4-cyclohexanedicarboxylate, 1-2 percent 1,4-cyclohexanedimethanol, and 1 percent methanol (Material Safety Data Sheet, Eastman Chemical Company, 2011). Only one limited study of biodegradation of MCHM is known, completed by Eastman Kodak Company of crude MCHM using a standard 28-day carbon dioxide (CO<sub>2</sub>) evolution test and laboratory-prepared water that was inoculated with activated sludge microorganisms previously unexposed to MCHM (Beglinger, 1997). The crude MCHM was classified as “not readily biodegradable” according to the test protocol because less than 60 percent biodegradation was measured within 10 days. Substantial CO<sub>2</sub> evolution was measured, however, after a 9-day lag period and indicated 53-54 percent degradation within the 28-day test period. If microorganisms used in this test had been previously exposed to MCHM, the lag period before degradation may not have occurred. Degradation products besides CO<sub>2</sub> were not measured, nor the relative amount of MCHM degradation compared to other components of the crude mixture. Recent controversy over reports of possible formaldehyde generation from crude MCHM released in the West Virginia spill demonstrate the need to evaluate both pure MCHM and the crude mixture.

Although alicyclic hydrocarbons are substantial components of petroleum mixtures, and thus are common contaminants, relatively few studies of their biodegradation under aerobic and anaerobic conditions have been reported (Rios-Hernandez et al., 2003). Based on the chemical structure of MCHM, it is likely that the primary alcohol is oxidized to corresponding aldehydes and carboxylic acid, producing intermediates such as 4-methylcyclohexanecarboxylic acid,

which is a naphthenic acid. Naphthenic acids are natural components of hydrocarbon deposits and their environmental fate and toxicity have been reviewed recently because they are major contaminants in extraction water from oil sands and other petroleum deposits (Headley and McMartin, 2004). Naphthenic acids generally are considered weakly biodegradable, although both aerobic and anaerobic cultures of native microbial communities from oil sands tailings water have been shown to be capable of degrading a range of these compounds (Headley and McMartin, 2004). Alkylsuccinate derivatives, in addition to carboxylic acid compounds, also have been identified as metabolites under sulfate-reducing conditions in a study that used ethylcyclopentane as a model alicyclic hydrocarbon (Rios-Hernandez et al., 2003).

We propose to characterize the biodegradation processes, rates, and metabolites using site water and sediment with native microbial communities potentially acclimated to crude MCHM from exposure at the Elk River spill site to the MCHM. Replicate microcosms would be prepared in the laboratory under a range of redox conditions, amended with crude MCHM, and monitored for loss of MCHM and production and removal of metabolites. Sterile controls also would be prepared to measure potential loss due to abiotic processes such as sorption. Samples collected from the site would be analyzed for metabolites observed in the laboratory to confirm their potential importance on environmental fate of MCHM. Microcosm preparation and analysis would be performed in the USGS Maryland-Delaware-DC research laboratory. A GC/MS with purge and trap and a GC/FID are available in this laboratory for analyses. Additional analytical support could be obtained from the USGS National Water Quality Laboratory for metabolite identification. Collection of samples for laboratory testing and confirmation analyses would be performed the USGS West Virginia Water Science Center.

### **References Cited**

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